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(54) Concrete product

(57) A process for the manufacture of concrete products from a concrete mixture is characterised in that the concrete mixture comprises a polymeric dispersion containing from 5 to 75% by weight, based on the dry polymer content, of at least one carboxylic acid ester, such as glycerine monooleate, ethyl oleate, diethylene glycol monooleate. Dry and semi-dry mix concrete products made according to the process are self-supporting in the uncured state and when cured have low water absorption characteristics and high impact resistance.

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Description

BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to a process for reducing the water permeability and at the same time improving the impact resistance of concrete products, especially concrete products made from dry and semi dry mixes.

2. Description of the prior art

The tendency of concrete products to absorb water can be reduced by designing the mix to have a low void content generated by the aggregates used in conjunction with an optimised cement content.

It is known that the water absorption can be further reduced by including a waterproofing agent in the mix but the addition needed to give a desired reduction results in a loss of compressive and impact strength characteristics.

It is also known to use water based polymeric emulsions to improve impact resistance and water repellency characteristics of concrete products but the level of addition required to achieve the desired water repellency does not allow the production of self supporting products when they are still in the wet, uncured state. In particular it has been found extremely difficult to produce dry mix products which comply with the initial water permeability requirement specified in BS 1217:1986 "Specification for Cast Stone" which states a maximum initial water absorption at one hour of not greater than 0.10 $mL/m^2.s$ to meet Grade A.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a process for the production of concrete products, especially dry and semi-dry mix concrete products, which possess good impact resistance and at the same time have a low water permeability characteristic in compliance with the initial water absorption requirement of BS 1217.

To this end, the present invention resides in a process for the production of concrete products wherein the original concrete mixture comprises a polymeric dispersion containing from 5 to 75% by weight, preferably 10 to 30% by weight, calculated relative to the dry polymer content, of at least one ester of a carboxylic acid.

The main advantages of the process according to the invention are that it can be used in the production of dry and semi dry concrete products that are self supporting in the uncured condition, that when fully cured have low water absorption characteristics in compliance with the initial water absorption requirement of BS 1217 and high impact resistance.

Examples of concrete products which can be beneficially manufactured according to the process include blocks, bricks, paviours, and cast and reconstituted stone.

Moreover, the manufactured concrete products may comprise a single concrete mixture according to the invention or may comprise several concrete mixtures of which one or more may be formulated according to the invention. One example of a product which may be beneficially made from more than one concrete mixture is a block comprising a bulk backing mix formed from a lightweight concrete having good thermal properties and a facing mix which is formulated according to the invention to impart the desired impact resistance and water absorption characteristics to the product. Preferably, the facing mix is formed in situ on the backing mix.

Advantageously, the polymeric dispersion used in accordance with the invention is an aqueous dispersion. Production of such an aqueous dispersion can be effected by simple mixing means, the esters being stirred into the dispersion due to their compatibility.

The ester is preferably mixed with the polymer dispersion and the dispersion then allowed to mature before addition to the concrete mix, the length of maturation being preferably from a few seconds to about seven days, and more preferably from fifteen minutes and twenty four hours. Moreover, it is preferred to add the matured polymeric dispersion to the concrete mix at the time of mixing the concrete components.

The carboxylic acid esters contained in the polymeric dispersion according to the invention are preferably derived from carboxylic acids having from 10 to 20 carbon atoms. These carboxylic acids are preferably monocarboxylic acids and may be saturated or singly or multiply unsaturated and straight or branched chain. Lauric, stearic, oleic and linoleic acids are particularly preferred.

The carboxylic acid esters are most preferably formed by the esterification reaction between carboxylic acids and alcohols, preferably primary or secondary alcohols, but of course they could equally be prepared by reaction between alcohols and acyl halides, amides or anhydrides or any other method. The alcohols may be monohydric or polyhydric.

Preferred alcohols for use in the esterification include methyl, ethyl and propyl alcohols, especially ethylene glycol, diethylene glycol and glycerine. In the case of polyhydric alcohols, not all the hydroxy groups need be esterified. More-

over, to facilitate processing, it is also preferred to use esters which are liquids at normal room temperatures. Examples of preferred esters include ethyl oleate, glycerine monooleate, ethylene glycol monooleate, ethylene glycol dioleate, diethlyene glycol dioleate and diethylene glycol monooleate.

Preferably, the polymeric dispersions used have an average particle size of from 0.02 to 2 microns, more preferably an average particle size of from 0.05 to 1.0 microns. The polymeric dispersions preferably have a solids content of between 20 and 75%, more preferably between 40 and 60%.

The polymer used to form the polymeric dispersion may be any suitable polymer, but acrylic or methacrylic polymers, styrene polymers and vinyl polymers are preferred. Particularly preferred are acrylic homopolymers and copolymers, styrene acrylic copolymers, styrene butadiene copolymers and homopolymers, copolymers and terpolymers of vinyl acetate.

The polymer dispersion is preferably added in an amount from 0.2 to 30% by weight of cement and more preferably in an amount of from 0.5 to 10% by weight of cement.

Any combination of suitable aggregates and cement may be used for the invention to be effective. Examples of suitable aggregates are sand, limestone, marble, calcined flint, and granite. Examples of suitable cements are Ordinary Portland, Rapid Hardening Ordinary Portland, White Portland, Sulphate Resisting Portland, Portland Blastfurnace, Portland Pulverised Fuel Ash, and High Alumina.

A number of examples are now provided to illustrate the invention, all parts and percentages expressed therein are by weight. The components used to form the concrete products and the test methods employed to measure the physical properties of the products are briefly described below.

Chelford sand is a glacial deposit of high silica sand of the Pleistocene period and arising at Lower Witherington, Cheshire, England. Chelford 50 is a particular fraction with a rounded shape and an average grain size of 275 microns. Chelford 95 is another particular fraction with a sub rounded shape and an average grain size of 145 microns.

One granite found suitable arises at Mountsorrel, Leicestershire, England having an angular shape and average grain size of 340 microns.

OP cement and White cement are Ordinary Portland Cement complying with BS 12, "Specification for Portland Cement".

The method employed to determine impact resistance involved the dropping through a guide tube of a ball of known mass from progressively increasing and known heights on to the corner of the concrete product until fracture occurred. The cumulative energy of the falling ball until the point of fracture was computed and reported as the impact resistance.

The Isat water absorption method involved the placement of a standing head of water on the concrete product for a period of 60 minutes followed by the immediate measurement by means of an manometer interconnecting with the standing head of water the continuing absorption of water into the concrete product. The rate was computed and reported as initial water absorption at 60 minutes in $mL/m^2.s$.

Example 1 (Standard)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	50 dJ/cm^2
Isat 60min absorption:	1.2 $mL/m^2.s$

Example 1(a)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
50% Styrene acrylic aqueous dispersion	0.75 parts
including glycerine mono oleate	0.02 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	200 dJ/cm^2
Isat 60min absorption:	0.12 mL/m^2.s

Example 1(b)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
50% Styrene acrylic aqueous dispersion	0.75 parts
including glycerine mono oleate	0.125 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	220 dJ/cm^2
Isat 60min absorption:	0.01 mL/m^2.s

Example 1(c)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts

50% Styrene acrylic aqueous dispersion	0.75 parts
including glycerine mono oleate	0.25 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	150 dJ/cm^2
Isat 60min absorption:	0.01 mL/m^2.s

Example 2 (Standard)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	50 dJ/cm^2
Isat 60min absorption:	1.2 mL/m^2.s

Example 2(a)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
46% Styrene butadiene dispersion	0.75 parts
including ethyl oleate	0.02 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	150 dJ/cm^2
Isat 60min absorption:	0.18 mL/m^2.s

Example 2(b)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
46% Styrene butadiene dispersion	0.75 parts
including ethyl oleate	0.125 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	150 dJ/cm^2
Isat 60min absorption:	0.03 mL/m^2.s

Example 2(c)

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
46% Styrene butadiene dispersion	0.75 parts
including ethyl oleate	0.25 parts
(Maturation time after mixing)	12 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	110 dJ/cm^2
Isat 60min absorption:	0.02 mL/m^2.s

Example 3 (Standard)

A concrete product was manufactured in accordance with the following formulation:

Mountsorrel granite	32 parts
Chelford 95 sand	16 parts
White Cement	16 parts
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	40 dJ/cm^2
Isat 60min absorption:	1.3 mL/m^2.s

Example 3(a)

A concrete product was manufactured in accordance with the following formulation:

Mountsorrel granite	32 parts
Chelford 95 sand	16 parts
White Cement	16 parts
48% Acrylic aqueous dispersion	0.75 parts
including diethylene glycol monooleate	0.02 parts
(Maturation time after mixing)	5 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	190 dJ/cm^2
Isat 60min absorption:	0.15 mL/m^2.s

Example 3(b)

A concrete product was manufactured in accordance with the following formulation:

Mountsorrel granite	32 parts
Chelford 95 sand	16 parts
White Cement	16 parts
48% Acrylic aqueous dispersion	0.75 parts
including diethylene glycol monooleate	0.125 parts
(Maturation time after mixing)	5 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. The resulting product had the following properties:

Impact resistance:	210 dJ/cm^2
Isat 60min absorption:	0.02 mL/m^2.s

Example 3(c)

A concrete product was manufactured in accordance with the following formulation:

Mountsorrel granite	32 parts
Chelford 95 sand	16 parts
White Cement	16 parts
48% Acrylic aqueous dispersion	0.75 parts
including diethylene glycol monooleate	0.25 parts

(continued)

(Maturation time after mixing)	5 hours
Water %	6.5

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. Products were tested with the following results:

Impact resistance:	170 dJ/cm^2
Isat 60min absorption:	0.01 mL/m^2.s

The following test series illustrate the effect of maturation of the polymer dispersion containing an ester according to the invention.

Example 4

A concrete product was manufactured in accordance with the following formulation:

Chelford 50 sand	32 parts
Chelford 95 sand	16 parts
OP Cement	16 parts
Water %	6.5
50% Styrene acrylic aqueous dispersion	0.75 parts
including glycerine mono oleate	0.125 parts
Maturation times after mixing according to table of results.	

The product was cured at 20°C and high humidity for 20 hours and for a further 27 days in normal air. Products were tested with the following results:

Maturity of the polymer dispersion before use	Impact Resistance dJ/cm^3	7 day Isat initial water absorption mL/m^2.s
30 seconds	230	0.09
5 minutes	220	0.04
15 minutes	220	0.01
1 hours	220	0.01
5 hours	220	0.01
12 hours	220	0.01
24 hours	220	0.01
7 days	210	0.02
28 days	190	0.08

While particular embodiments have been described, it should be appreciated that various modifications may be

made without departing from the scope of the invention.

Claims

1. A process for the manufacture of a concrete product from a concrete mixture wherein said concrete mixture comprises a polymeric dispersion containing from 5 to 75% by weight, based on the dry polymer content, of at least one carboxylic acid ester.

2. A process according to claim 1 wherein said polymeric dispersion is an aqueous dispersion.

3. A process according to claim 1 or 2 wherein said concrete mix is a dry or semi-dry mix.

4. A process according to any preceding claim wherein said carboxylic acid ester is derived from a monocarboxylic acid.

5. A process according to any preceding claim wherein said carboxylic acid ester is derived from a carboxylic acid containing from about 10 to about 20 carbon atoms.

6. A process according to claim 4 or 5 wherein said carboxylic acid is selected from lauric, stearic, oleic and linoleic acid.

7. A process according to any preceding claim wherein said carboxylic acid ester is derived from a methyl, ethyl or propyl alcohol.

8. A process according to claim 7 wherein said carboxylic acid ester is derived from ethylene glycol, diethylene glycol or glycerine.

9. A process according to any preceding claim wherein said carboxylic acid ester comprises ethyl oleate, ethylene glycol monooleate, ethylene glycol dioleate, diethylene glycol monooleate, diethylene glycol dioleate or glycerine monooleate.

10. A process as claimed in any preceding claim wherein said polymeric dispersion contains from 10 to 30% by weight of said ester, calculated relative to the dry polymer content.

11. A process as claimed in any preceding claim wherein said polymeric dispersion is comprised of particles having an average particle size of from 0.02 to 2 microns.

12. A process as claimed in claim 11 wherein the particles in said polymeric dispersion have an average particle size of from 0.05 to 1.0 microns.

13. A process as claimed in any preceding claim wherein said polymeric dispersion has a solids content of from about 20 to 75%.

14. A process as claimed in claim 13 wherein said polymeric dispersion has a solids content of from about 40 to 60%.

15. A process as claimed in any preceding claim wherein said polymeric dispersion comprises an acrylic or methacrylic polymer, a styrene polymer, a butadiene polymer or a vinyl polymer.

16. A process according to claim 15 wherein said polymeric dispersion comprises an acrylic homopolymer or copolymer.

17. A process according to claim 16 wherein said polymeric dispersion comprises a styrene acrylic copolymer.

18. A process according to claim 15 wherein said polymeric dispersion comprises a styrene butadiene copolymer.

19. A process according to claim 15 wherein said polymeric dispersion comprises a homopolymer, copolymer or terpolymer of vinyl acetate.

20. A process as claimed in any preceding claim wherein said polymeric dispersion is added in an amount of from 0.2 to 30% by weight of cement.

21. A process as claimed in claim 20 wherein said polymeric dispersion is added in an amount of from 0.5 to 10% by weight of cement.

22. A process as claimed in any preceding claim wherein said polymer dispersion containing an ester has been allowed to maturate for a period of from about 15 minutes to about 24 hours.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 9166

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE-A-32 35 095 (SUMITOMO CHEMICAL CO) * page 7, line 8 - line 22 * * page 9, line 10 - line 15 * * page 10, line 2 - line 9; claim 1 * ---	1-8,10, 13-15, 19,21	C04B28/02 //(C04B28/02, 24:04,24:26), (C04B28/02, 24:08,24:26)
X	EP-A-0 342 609 (AIR PRODUCTS AND CHEMICALS INC.) * abstract * * page 3, line 41 - line 53 * ---	1,2,4-6, 10, 13-16, 19-21	
A	US-A-3 043 790 (PH. F. SANDERS ET AL.) * column 2, line 16 - line 27; claim 1 * ---	1,2, 4-10,15, 18,20,21	
A	FR-A-1 526 324 (P. EGOT ET AL.) * claims * ---		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	GB-A-938 567 (SHAWINIGAN RESINS CORP.) * claims 1,15 * -----		C04B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 April 1996	Daeleman, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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